

Chapter 1

Foundations

1.1 Introduction

A macroscopic system is, typically, composed of the order of 10^{23} particles. It is impossible to know, investigate, or describe the exact microscopic behaviour of *each* individual particle in such a system. We must limit our knowledge to the average properties, *thermodynamic quantities* like the temperature or pressure and *correlation functions*.

Statistical mechanics is the bridge between the *microscopic* and *macroscopic* world, it provides methods of calculating the macroscopic properties, like the specific heat, from the microscopic information, like the interaction energy between the particles. The essential ingredient of statistical mechanics is the *probability distribution*, i.e., the collection of occupancies of different *configurations* (microscopic states).

Phase Space. Consider as an example the ideal gas of N particles in a three-dimensional space. The Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i,j \neq i} V_{ij}; \quad V_{ij} \rightarrow 0. \quad (1.1)$$

(p_i is the component of the momentum, m is the particle mass, and V_{ij} the interaction between particles. The interaction term is necessary for the system of particles to reach thermal equilibrium, but it can be neglected compared to the kinetic energy.). The $3N$ coordinates and $3N$ momenta form the $6N$ dimensional *phase space*. Each point in the phase space represents a *microscopic* state of the

system. The microscopic state changes in time according to the canonical equations of motion:

$$\dot{p}_j = -\frac{\partial \mathcal{H}}{\partial q_j} \quad \text{and} \quad \dot{q}_j = \frac{\partial \mathcal{H}}{\partial p_j}. \quad (1.2)$$

and traces a *trajectory* in the phase space.

Ensembles. The system is completely described if we know the coordinates and momenta of all particles ($6N$ variables - a terrible task). To get an *average* of a physical quantity, say A , one should make the time average over a long segment of the trajectory (a collection of consecutive configurations) of such a system in the phase space,

$$\langle A \rangle = \lim_{\Delta t \rightarrow \infty} \frac{1}{\Delta t} \int_{t_0}^{t_0 + \Delta t} A[\{q_i(t), p_i(t)\}] dt. \quad (1.3)$$

However, usually we know neither the exact microscopic state, i.e., the location of the system in the phase space, nor the trajectory. What we can know, is the macroscopic state (temperature, pressure, volume, ...). Instead of studying a particular microscopic state and the trajectory over the phase space, we investigate an *ensemble of systems*, i.e., a collection of all possible microscopic systems, all belonging to the same macroscopic state.

Ergodicity. To calculate the average of a physical quantity, we substitute the time average over one system by an average over an ensemble of equivalent systems at fixed time:

$$\langle A \rangle = \int_W A(\{q_i, p_i\}) p(\{q_i, p_i\}) d^{3N} q d^{3N} p. \quad (1.4)$$

The integral is over the whole phase space W and p is the probability density in the phase space, it is the probability that a unit volume of the phase space is occupied. So, instead of the *time average*, we make an *ensemble average at fixed time*. When the time and the ensemble averages are equal, we say that the system is *ergodic*. In an alternative but equivalent definition we say that a system is ergodic if it evolves in such a way that it visits with *equal probability* all points of the phase space which are accessible from the initial configuration subject to the constraint of energy conservation. In other words, the trajectory in the phase space of an ergodic system will spend equal time intervals in all regions of the constant energy surface. Most of the physical systems of interest in statistical mechanics are ergodic, so we will in most of the cases replace time averages by the corresponding ensemble averages.

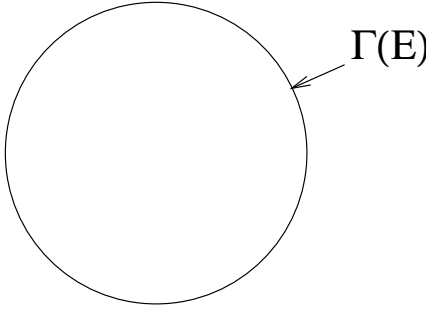


Figure 1.1: Constant-energy surface in the phase space. The area of the surface in the $6N$ -dimensional phase space is $\Gamma(E)$.

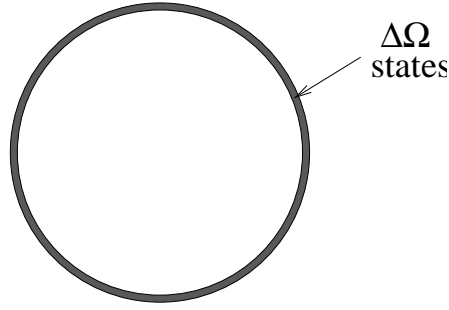


Figure 1.2: Constant-energy shell in the $6N$ -dimensional phase space. The number of states in the shell is $\Delta\Omega(E)$.

For the above example of an isolated ideal gas, the total energy of the system is constant, $\mathcal{H} = E$, the trajectory lies on the constant-energy surface $\Gamma(E)$ in the phase space and the ensemble average of A is:

$$\langle A \rangle = \frac{1}{\Gamma(E)} \int_{\Gamma(E)} A(\{q_i, p_i\}) d^{3N}q d^{3N}p. \quad (1.5)$$

(The integral is over the constant energy surface $\Gamma(E)$.) For quantum systems as well as for classical systems with discrete energy levels, the number of configurations is an extremely irregular function of the energy E . Therefore we introduce a narrow energy interval of the width ΔE and the ergodic hypothesis is generalized so that all the configurations, satisfying the condition that their energy is in the interval between E and $E + \Delta E$, are equally likely to occur. The number of configurations $\Delta\Omega$ with the energy in the interval between E and $E + \Delta E$ is proportional to the volume of the corresponding shell in the phase space. For indistinguishable particles, $\Delta\Omega$ is:

$$\Delta\Omega(E) = \frac{1}{h^{3N} N!} \sum_{E \leq \mathcal{H} \leq E + \Delta E} 1. \quad (1.6)$$

In principle, all systems in Nature obey *quantum statistical mechanics*, the energy levels are discrete, identical particles are indistinguishable and their wave-functions are either symmetric (Bosons) or antisymmetric (Fermions) upon exchange of two particles. *Classical statistical mechanics* is valid only as a special, limiting case when the average occupation of *any* single-particle quantum state is $\ll 1$.

Although we will discuss only statistical mechanics of systems in equilibrium, *i.e.*, *equilibrium statistical mechanics*, there is a growing interest in *nonequilibrium statistical mechanics* which investigates *steady, stationary* states of nonequilibrium systems.

1.2 Ensembles in Statistical Mechanics

An ensemble is a collection of many configurations of a system, all describing the same thermodynamic state. We start with a discussion of isolated systems.

1.2.1 Microcanonical Ensemble and the Entropy (Isolated Systems)

A microcanonical ensemble represents a collection of configurations of isolated systems that have reached thermal equilibrium. A system is isolated from its environment if it exchanges neither particles nor energy with its surrounding. The volume, internal energy and number of particles of such a system are constant and are the same for all configurations that are part of the same microcanonical ensemble. Instead of working with constant energy surface $\Gamma(E)$, we consider all the states with the total energy in a narrow energy interval between E and $E + \Delta E$. All such configurations are lying in a thin shell in the phase space and the total number of configurations is $\Delta\Omega$.

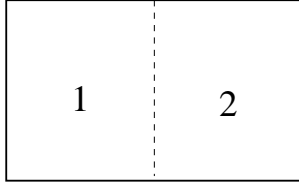
Closely related to the ergodic hypothesis is the *postulate of equal weights* which says that in equilibrium of an isolated system, *all the configurations with equal energy are equally probable*. For a system, belonging to a microcanonical ensemble, therefore, the probability for being in a configuration q_i, p_i with the energy $\mathcal{H}(\{q_i, p_i\})$ is:

$$p(\{q_i, p_i\}) = \begin{cases} 1/\Delta\Omega(E) & E \leq \mathcal{H}(\{q_i, p_i\}) \leq E + \Delta E \\ 0 & \text{otherwise.} \end{cases} \quad (1.7)$$

$\Delta\Omega(E)$ is the number of configurations having the energy in the interval $E \leq \mathcal{H}(\{q_i, p_i\}) \leq E + \Delta E$. All configurations $\{q_i, p_i\}$ which fall into this energy interval are occupied with equal probability $p(\{q_i, p_i\})$.

Entropy and Probability

Probably the most fundamental thermodynamic quantity in statistical physics is the *entropy*. Entropy is a concept, defined only for *macroscopic* systems. A system of only a few particles does not have an entropy. The entropy is a measure of disorder in the system. and is an *additive function of state*.



Let us consider an isolated system composed of two subsystems, which are in contact with each other so that they can exchange energy and particles. As a result of the contact between the two subsystems, an additional uncertainty has been introduced into the

system (at the beginning we knew the energy and the number of particles of each individual subsystem, at the end we know only the total energy and number of particles of the whole system).

We *postulate* that the entropy is The entropy is an additive quantity, therefore:

$$S = S_1 + S_2 \quad (1.8)$$

We *postulate* that the entropy is

$$S = k_B \ln \Delta\Omega. \quad (1.9)$$

This relation was discovered by Ludwig Boltzmann and is therefore called the Boltzmann equation. The proportionality constant k_B is the Boltzmann constant and is determined by relating the statistical definition of the entropy to the thermodynamic definition. The Boltzmann equation provides the bridge between thermodynamics (entropy) and statistical mechanics (number of configurations).

The entropy plays the role of thermodynamic potential for microcanonical ensembles, $(-S)$ is minimal for an isolated system in equilibrium (V , E and N are kept constant). From thermodynamics we know that the total differential of the entropy is:

$$TdS(E, V, N) = dE + P dV - \mu dN. \quad (1.10)$$

(This is the *first law of thermodynamics*.) This equation provides a *statistical definition* of the temperature T , pressure P and chemical potential μ :

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V}, \quad (1.11)$$

$$P = T \left(\frac{\partial S}{\partial V} \right)_{N,E}, \quad (1.12)$$

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{E,V}. \quad (1.13)$$

T , p and μ are *intensive* quantities, they are independent of N whereas the entropy and the energy E are *extensive* quantities, they are proportional to the number of particles N .

1.2.2 Canonical Ensemble and the Free Energy (Systems at Fixed Temperature)

A *canonical ensemble* is a collection of closed systems at constant temperature. Closed systems have fixed number of particles and volume but can exchange energy with their surroundings. The energy of a closed system is therefore not constant. As an example we can imagine a gas of particles (air molecules, e.g.) in a closed container at constant temperature.

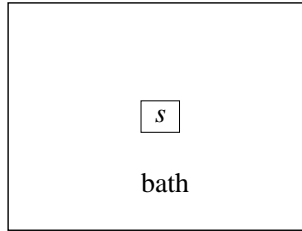


Figure 1.3: A small closed system (s) in contact with a large system, called “bath.” s and bath can exchange energy.

Consider now an isolated system composed of a small closed (sub)system s with N particles in a volume V and of a “heat bath” (b) at temperature T . Let the two subsystems be in contact so that they can exchange energy but no particles. In equilibrium, the system s has equal temperature as the heat bath. Now, the energy of the small system, E_s , is no longer fixed and the system s will be in any energy state E_s , in each one with a different probability p_s . The heat bath must be large ($N_b \gg N_s$), so that the change in the energy of the bath, E_b , during energy exchange between the small system and the bath, is negligible. Evidently, since the compound system (= system + bath) is isolated, the total energy $E_t = E_b + E_s$ is constant and the compound system belongs to a microcanonical ensemble for which the number of configurations in the energy interval between E_t and $E_t + \Delta E$ is:

$$\Delta\Omega_t(E_t) = \Delta\Omega_s(E_s)\Delta\Omega_b(E_t - E_s). \quad (1.14)$$

We first express $\Delta\Omega_b$ with the entropy via the Boltzmann equation (1.9) and then expand $\ln \Delta\Omega_b$ to first order in E_s :

$$k_B \ln \Delta\Omega_b(E_t - E_s) = S_b(E_t - E_s) \approx S_b(E_t) - \left(\frac{\partial S_b}{\partial E} \right) E_s = S_b(E_t) - \frac{E_s}{T}. \quad (1.15)$$

Thus,

$$\Delta\Omega_b(E_t - E_s) = \Delta\Omega_b(E_t) e^{-\beta E_s} = C e^{-\beta E_s}. \quad (1.16)$$

Here, the constant C is independent of E_s and β is the inverse temperature, $\beta = 1/k_B T$.

The (normalized) *probability* for the system s having the energy between E_s and $E_s + dE_s$ is:

$$p(E_s) dE_s = \frac{\Delta\Omega_s(E_s) \Delta\Omega_b(E_t - E_s) dE_s}{\int dE_s \Delta\Omega_s(E_s) \Delta\Omega_b(E_t - E_s)}. \quad (1.17)$$

After expressing $\Delta\Omega_b(E_t - E_s)$ with (1.16) we find the *probability density*:

$$p(E_s) = \frac{1}{Z} \rho(E_s) e^{-\beta E_s}, \quad (1.18)$$

where $\rho(E_s) = \Delta\Omega(E_s)/\Delta E$ is the density of states (number of states per unit energy interval). Z is called the *partition function* and is the normalization constant, depending on the temperature, volume and number of particles of the system s :

$$Z(T, V, N) = \int \rho(E) e^{-\beta E} dE. \quad (1.19)$$

(Here we omit the index s .) $Z(T, V, N)$ is a Laplace transform of the microcanonical partition function $\Delta\Omega(E) = \rho(E) \Delta E$. For systems with discrete energy levels we replace the integral either by a sum over all the energy levels l :

$$Z(T, V, N) = \sum_l g_l e^{-\beta E_l} \quad (1.20)$$

(g_l is the degeneracy of the energy level l), or by a sum over all configurations i :

$$Z(T, V, N) = \sum_i e^{-\beta E_i}. \quad (1.21)$$

The role of Z is much more important than just being the normalization constant. Z is obtained by integration over the whole phase space. In this way information on microscopic states of the system (coordinates and momenta of individual particles, e.g.) becomes lost but all thermodynamic information on the system (with prescribed temperature, number of particles and volume) is retained and can be obtained from Z , as we shall see below.

The distribution in which the particles are in equilibrium with a heat bath at temperature T is called a canonical distribution similarly as the ensemble defined by this distribution is called a *canonical ensemble*. For a system in equilibrium at a fixed temperature, the system can (at least in principle) access any energy. The probability density $p(E)$ is the same for all states with the same energy but it decreases exponentially with increasing energy.

Free Energy

In this Section we will see the relation between the average of a physical quantity of a canonical ensemble and the partition function Z .

The average energy $\langle E \rangle$ and average generalized force $\langle X \rangle$ in a canonical distribution are given by

$$\langle E \rangle = \frac{1}{Z} \int E \rho(E) e^{-\beta E} dE = -\frac{\partial}{\partial \beta} \ln Z, \quad (1.22)$$

$$\langle X \rangle = \frac{1}{Z} \int X \rho(E) e^{-\beta E} dE = \int \frac{\partial E}{\partial x} e^{-\beta E} dE = -\frac{\partial}{\partial x} \frac{1}{\beta} \ln Z. \quad (1.23)$$

x is the generalized coordinate, conjugate to the generalized force. Examples of conjugate forces and coordinates are: pressure vs. volume in gases, magnetic field vs. magnetization in magnetic systems; the generalized force is intensive while the coordinate is an extensive quantity.

We introduce the (Helmholtz) *free energy* as:

$$F(T, V, N) = -k_B T \ln Z(T, V, N). \quad (1.24)$$

Like the Boltzmann equation (1.9) in case of the microcanonical ensemble, also this equation relates thermodynamics (free energy) and statistical mechanics (partition function).

Relation between F and S : We take the well-known relation from thermodynamics:

$$F(T, V, N) = \langle E(S, V, N) \rangle - TS, \quad (1.25)$$

$F(T, V, N)$ is a Legendre transform of $\langle E(S, V, N) \rangle$, by which the independent variables are changed from (S, V, N) to (T, V, N) .

The total differential of F is:

$$dF = -SdT - PdV + \mu dN. \quad (1.26)$$

Another Legendre transform relates the Helmholtz and the Gibbs free energies $F(T, V, N)$ and $G(T, P, N)$:

$$G(T, P, N) = F(T, V, N) + PV \quad (1.27)$$

For a list of thermodynamic functions and their derivatives, see Tables 1 to 3 in the Appendix B. Exercise: Construct these tables for magnetic systems!

Stability and convexity of the free energies (See Fig. 1.4). The Helmholtz free energy $F(T, V)$ (for simplicity, we will omit N) is a concave (i.e, the second derivative is negative) function of T and convex function of V and the Gibbs free energy $G(T, P)$ is always a concave function of both T and P .

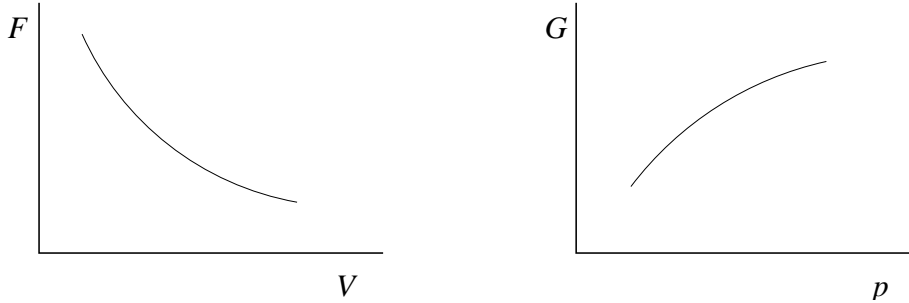


Figure 1.4: Schematic behaviour of the Helmholtz and Gibbs free energies.

These properties follow from the fact that the system must be thermally and mechanically stable, therefore the specific heat and the compressibility must be positive quantities. We begin by noting that

$$S = -\left(\frac{\partial G}{\partial T}\right)_p = -\left(\frac{\partial F}{\partial T}\right)_V. \quad (1.28)$$

It follows that

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\left(\frac{\partial S}{\partial T}\right)_p \equiv -\frac{1}{T}C_p \leq 0 \quad (1.29)$$

and

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_V = -\left(\frac{\partial S}{\partial T}\right)_V \equiv -\frac{1}{T}C_V \leq 0. \quad (1.30)$$

Hence, $G(T, p)$ and $F(T, V)$ are concave functions of T .

Together with equation (1.26) we see that for a system in equilibrium at constant T, V, N the distribution of a system over possible configurations is such that F is *minimal*. Therefore F is also called canonical or Gibbs *potential*.

The next two properties are obtained by differentiating $G(T, P)$ and $F(T, V)$ with respect to pressure and volume, respectively:

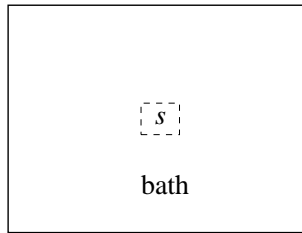
$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T \equiv -V\kappa_T \leq 0 \quad (1.31)$$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T = -\left(\frac{\partial P}{\partial V}\right)_T \equiv \frac{1}{V\kappa_T} \geq 0. \quad (1.32)$$

Hence, $G(T, P)$ is a concave function of pressure P and $F(T, V)$ is a convex function of volume V .

The above properties are valid also for systems that undergo phase transitions.

1.2.3 Grand Canonical Ensemble (Open systems)



Consider now a more general case with the system of volume V_s being not only in contact with a heat bath at temperature T , but also exchanging particles with the bath. As an example we can imagine a room at constant temperature with an open window. In this case, neither the energy nor the number of particles in the system (air molecules in the room, e.g.) are fixed. Such a system is described by the *grand canonical distribution*.

We proceed like in case of the canonical ensemble, we consider the total system being part of a microcanonical ensemble, therefore the number of configurations of the total system is:

$$\Delta\Omega(E_t, N_t) = \Delta\Omega_s(E_s, N_s) \Delta\Omega_b(E_t - E_s, N_t - N_s). \quad (1.33)$$

We express $\Delta\Omega_b$ with the entropy via the Boltzmann equation and then expand $\ln \Delta\Omega_b$ to first order in E_s and N_s :

$$\begin{aligned} k_B \ln \Delta\Omega_b(E_t - E_s, N_t - N_s) &= S_b(E_t - E_s, N_t - N_s) \\ &\approx S_b(E_t, N_t) - \left(\frac{\partial S_b}{\partial E} \right) E_s - \left(\frac{\partial S_b}{\partial N} \right) N_s \\ &= S_b(E_t, N_t) - \frac{E_s}{T} + \frac{\mu N_s}{T}. \end{aligned}$$

Thus,

$$\Delta\Omega_b(E_t - E_s, N_t - N_s) = C e^{-\beta(E_s - \mu N_s)}. \quad (1.34)$$

Eventually we find for the probability density of a system having the energy E and N particles:

$$p(E, N) = \frac{1}{\Xi} \rho(E, N) e^{-\beta(E - \mu N)}, \quad (1.35)$$

where the normalization constant Ξ is called the *grand (canonical) partition function*:

$$\Xi(T, V, \mu) = \sum_N \int \rho(E, N) e^{-\beta(E - \mu N)} dE. \quad (1.36)$$

(Again, we omit the index s .) The grand partition function Ξ is related to the partition function Z :

$$\Xi(T, V, \mu) = \sum_N Z(T, V, N) e^{\beta\mu N}. \quad (1.37)$$

Thermodynamic quantities in the grand canonical ensemble

In analogy to the free energy in the case of a canonical ensemble, we introduce the grand (canonical) potential J which will be used for open systems:

$$J(T, V, \mu) = -k_B T \ln \Xi \quad (1.38)$$

The total differential of J is:

$$dJ = -SdT - pdV - Nd\mu. \quad (1.39)$$

The entropy can now be expressed as

$$S = - \left(\frac{\partial J}{\partial T} \right)_{V, \mu} = k_B \ln \Xi + k_B T \left(\frac{\partial \ln \Xi}{\partial T} \right)_{V, \mu}, \quad (1.40)$$

the pressure is:

$$p = -\left(\frac{\partial J}{\partial V}\right)_{T,\mu} = k_B T \left(\frac{\partial \ln \Xi}{\partial V}\right)_{T,\mu}, \quad (1.41)$$

and the number of particles is

$$N = -\left(\frac{\partial J}{\partial \mu}\right)_{T,V} = k_B T \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{T,V}. \quad (1.42)$$

For a system in equilibrium at constant T , V , and μ , the distribution of a system over possible configurations is such that the potential J is minimal.

1.3 Analogy Between Fluids and Magnetic Systems

Above, we have mainly discussed fluids (liquids, gases). When we want to consider, e.g., magnetic systems, the above relations between thermodynamic quantities are easily written down for them as well. The potential energy of a magnetic dipole μ in a magnetic field H is

$$W = -\mu H \quad (1.43)$$

and the work required to increase the magnetization of a system by dM is:

$$-H d\mu. \quad (1.44)$$

Hence, the first law of thermodynamics for magnets reads:

$$T dS = dE - H dM \quad (1.45)$$

Comparing this equation with 1.10 we see that we only have to replace the "generalized force" - pressure P by the "force", acting on the magnetic moment, i.e., by the negative magnetic field:

$p \rightarrow -H.$

(1.46)

Similarly, the "generalized coordinate" V is replaced by the "generalized coordinate" of magnetic systems, M :

$V \rightarrow M.$

(1.47)

Notice that P and H are intensive quantities whereas V and M are extensive.

1.4 Fluctuations

The microcanonical ensemble describes a collection of isolated systems where neither energy nor the number of particles can fluctuate.

Energy fluctuations in the canonical ensemble: The canonical ensemble describes a system in contact with a heat bath. For such a system, the energy is not exactly fixed, it can fluctuate around $\langle E \rangle$. We will now evaluate the square of the energy fluctuations,

$$(\Delta E)^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2. \quad (1.48)$$

In the canonical ensemble, the thermal average of the energy is

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad (1.49)$$

and the thermal average of the energy squared is:

$$\langle E^2 \rangle = \frac{1}{Z} \int E^2 \rho(E) e^{-\beta E} dE = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}. \quad (1.50)$$

So, the square of the energy fluctuation is

$$(\Delta E)^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}. \quad (1.51)$$

After expressing this with $\langle E \rangle$ (see paragraph 2.3.3) we get:

$$(\Delta E)^2 = -\frac{\partial \langle E \rangle}{\partial \beta} = k_B T^2 \frac{\partial \langle E \rangle}{\partial T}. \quad (1.52)$$

$$(\Delta E)^2 = k_B T^2 C_V. \quad (1.53)$$

Here, C_V is the *heat capacity*, it is an extensive quantity and is proportional to N . The relative fluctuation of the energy is thus:

$$\frac{\Delta E}{\langle E \rangle} = \sqrt{\frac{k_B c_V}{N}} \frac{T}{\varepsilon}, \quad (1.54)$$

where ε is the energy per particle and c_V is the specific heat at constant volume, $c_V = C_V/N$. The relative energy fluctuation is $\propto 1/\sqrt{N}$ and it vanishes as $N \rightarrow \infty$, see Fig. 1.5. For macroscopic systems (i.e., in the limit $N \rightarrow \infty$), the

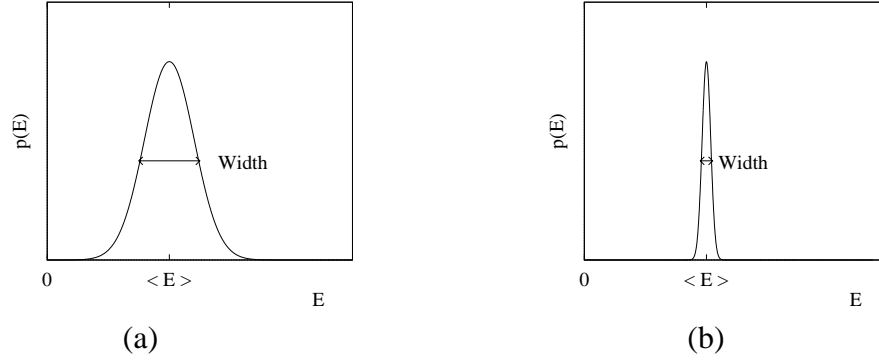


Figure 1.5: Fluctuation in the energy of a small (a) and of a large (b) system.

distribution of energies in a canonical ensemble is so sharply peaked around the average energy that the *canonical ensemble is equivalent to the microcanonical ensemble*. For later use we write Eq. (1.54) in the form:

$$c_v = \frac{\beta}{NT} \left(\langle E^2 \rangle - \langle E \rangle^2 \right) \quad (1.55)$$

Fluctuations in the grand canonical ensemble: Now the number of particles is not fixed, so we shall calculate ΔN (and ΔE). The calculation is analogous to the above calculation for the canonical ensemble. We start with the grand partition function

$$\Xi(T, V, \mu) = \sum_N \int \rho(E) e^{-\beta(E - \mu N)} dE \quad (1.56)$$

and differentiate it twice with respect to μ by keeping β and V constant,

$$\langle N \rangle = \frac{1}{\beta \Xi} \frac{\partial \Xi}{\partial (\mu)}, \quad (1.57)$$

$$\langle N^2 \rangle = \frac{1}{\beta^2 \Xi} \frac{\partial^2 \Xi}{\partial \mu^2}. \quad (1.58)$$

The square of the particle number fluctuation is:

$$(\Delta N)^2 = \langle N^2 \rangle - \langle N \rangle^2 = \left(\frac{\partial^2 \ln \Xi}{\beta^2 \partial \mu^2} \right)_{T,V}. \quad (1.59)$$

For fluids at constant T and V , we obtain from the thermodynamic relation (See Table 1) $pV = k_B T \ln \Xi$:

$$\frac{\partial^2 \ln \Xi}{\partial \mu^2} = \frac{V}{k_B T} \frac{\partial^2 p}{\partial \mu^2}. \quad (1.60)$$

We assume that the (Helmholtz) free energy can be written as $F(T, V, N) = N f(T, v)$, where $f(T, v)$ is the free energy per particle and depends on T and $v \equiv V/N$. Then,

$$\mu(T, p) = f(T, v) + pv \quad (1.61)$$

and

$$\frac{\partial^2 p}{\partial \mu^2} = \frac{\partial}{\partial \mu} \left(\frac{1}{v} \right) = -\frac{1}{v^2} \frac{\partial v}{\partial \mu}, \quad (1.62)$$

where

$$\frac{\partial \mu}{\partial v} = \frac{\partial \mu}{\partial p} \frac{\partial p}{\partial v} = v \frac{\partial p}{\partial v} \equiv -\frac{1}{\kappa_T}. \quad (1.63)$$

κ_T is the isothermal compressibility. We get finally that

$$\langle N^2 \rangle - \langle N \rangle^2 = \frac{\langle N \rangle k_B T \kappa_T}{v}. \quad (1.64)$$

The square of the fluctuation in the number of particles is proportional to the (isothermal) compressibility! This equation shows also that $\Delta N \propto \sqrt{N}$ and that $\Delta N / \langle N \rangle$ vanishes as $N \rightarrow \infty$. We conclude that the grand canonical ensemble is equivalent to the canonical ensemble when $\langle N \rangle \rightarrow \infty$. The decision about which ensemble is to be used to describe the investigated system does not depend on whether the system is closed or open, but it is a matter of convenience. For later use we rewrite Eq. 1.64 in a different form:

$$\kappa_T = \frac{v\beta}{\langle N \rangle} \left(\langle N^2 \rangle - \langle N \rangle^2 \right) \quad (1.65)$$

The limit $N \rightarrow \infty$, in which the relative fluctuations become negligible, is called the *thermodynamic limit*. So far we assumed c_V or κ_T to be constant. At a continuous phase transition however (see Section 1.5), these quantities and consequently also the corresponding fluctuations diverge on *all lengthscales*. This makes life of experimentalists and of those who make simulations on computers (both can deal with finite systems only) very difficult.

The fluctuations of N around $\langle N \rangle$ or E around $\langle E \rangle$ are - of course - time-dependent processes! Therefore we have to assume that the systems are ergodic in order to identify the *time average* with an *ensemble average* which we actually calculated.

Fluctuation-Dissipation Theorem

Above, we have shown that $(\Delta E)^2$ is proportional to the specific heat c_V and that $(\Delta N)^2$ is proportional to the compressibility. In the problem 3 we also see that $(\Delta M)^2$ is proportional to the susceptibility. All these examples indicate that there is a general relation between the *fluctuations* of the generalized coordinate and the *response* of this coordinate to the perturbation of the conjugate generalized force.

This is the message of the *fluctuation-dissipation theorem* which in a most general way relates the fluctuations of a physical quantity of a system in equilibrium to a dissipation process which is realized when the system is subject to an external force driving it away from equilibrium. The theorem makes it possible to find the *non-equilibrium* properties of a system from the analysis of thermal fluctuations of the system in *equilibrium*. It is a bridge between non-equilibrium and equilibrium statistical mechanics.

Now let us have a look at magnetic systems. The magnetic susceptibility, i.e., the response of the magnetization M to the external magnetic field H is:

$$\chi = \frac{\beta}{N} (\langle M^2 \rangle - \langle M \rangle^2). \quad (1.66)$$

If we write $M = \sum_i S_i$, the susceptibility becomes:

$$\chi = \frac{\beta}{N} \sum_{i,j} [\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle]. \quad (1.67)$$

The summand on the right-hand side is the spin-spin *correlation function*,

$$\Gamma_{ij} = [\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle]. \quad (1.68)$$

which describes the correlations in the spatial fluctuations of the spin around its thermal average. Because of the interaction between the nearest-neighbouring spins, one expects that the spins are *correlated* on short distances and that their fluctuations are less and less correlated as the distance increases. The correlation function thus decays with the distance. Often Γ will be assumed to have the form

$$\Gamma(r) \propto r^{-p} e^{-r/\xi}, \quad (1.69)$$

where the decay length ξ is called the *correlation length*. As we shall see later, ξ is a temperature-dependent quantity which plays a crucial role in phase transitions, it diverges at a continuous phase transition.

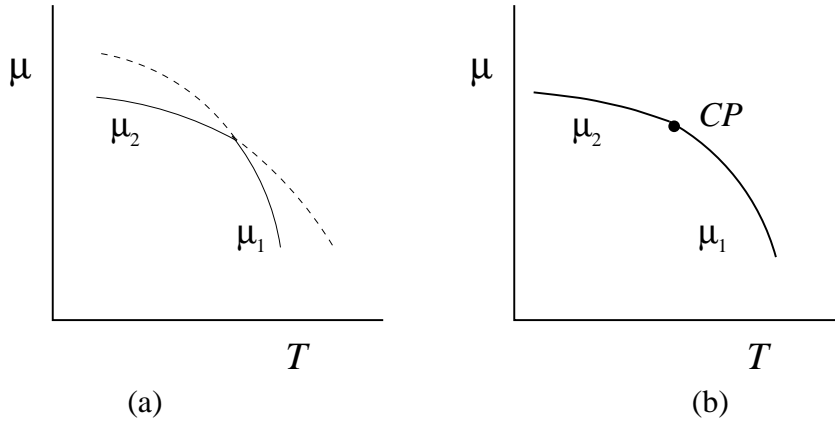


Figure 1.6: Chemical potentials of two phases in contact. When $\mu_1 = \mu_2$, the two phases coexist. In figure (a) the chemical potentials cross and the transition is first order. Dashed portions represent unstable states. In figure (b) the transition is continuous and the two phases meet in the critical point CP .

1.5 Phase Transitions

So far we have considered only homogeneous systems, i.e., single phases. In Nature there are, however, many systems that exist in different phases. Examples are solid-liquid-gas, magnetic, ferroelectric, \dots , systems. In this Section we will discuss transitions between such phases.

When two phases, say 1 and 2 are in contact with each other, there is an *interface* separating the phases. In equilibrium, the chemical potentials of both phases in contact are equal,

$$\mu_1(T, p_1, \dots) = \mu_2(T, p_2, \dots) \quad (1.70)$$

and the two phases *coexist* (See Figure 1.6).

Classification of Phase Transitions

As one of the parameters (e.g., the temperature) is varied in such a way that the coexistence line is crossed, the system undergoes a *phase transition* between the two phases. At the phase transition a derivative of the free energy (or some other

thermodynamic potential) is discontinuous. The free energy (thermodynamic potential) becomes non-analytic in this point. The transition can be either *first order* or *continuous*.

(a) *First-order phase transitions*. The conditions for first-order phase transitions are that the chemical potentials are equal,

$$\Delta\mu = \mu_1(T, p, \dots) - \mu_2(T, p, \dots) = 0, \quad (1.71)$$

and that their derivatives are different,

$$\frac{\partial\Delta\mu}{\partial T} \neq 0 \quad \text{and} \quad \frac{\partial\Delta\mu}{\partial p} \neq 0, \quad (1.72)$$

so that the chemical potentials or the free energies *cross* at the transition. The phase with the lower chemical potential is *stable* and the other phase is *metastable*. An example of a first-order phase transition is the liquid-gas transition.

(b) *Continuous phase transitions*. A transition is continuous when the chemical potentials of both phases are equal and when their first derivatives are also equal,

$$\Delta\mu = \mu_1(T, p, \dots) - \mu_2(T, p, \dots) = 0, \quad (1.73)$$

$$\frac{\partial\Delta\mu}{\partial T} = 0 \quad \text{and} \quad \frac{\partial\Delta\mu}{\partial p} = 0, \quad (1.74)$$

so that the chemical potentials or the free energies have a common tangent at the transition. There is no latent heat in this type of transition.

Instead of continuous transitions, some authors write about *second*, *third*, and higher order transitions, depending on which derivative of the chemical potential diverges or becomes discontinuous. This classification is somewhat arbitrary, therefore we will distinguish only between the continuous and first-order transitions.

1.5.1 Order Parameter

As an example, let us consider a simple ferromagnetic material. At high temperatures, there is no magnetization and the system is rotationally invariant. At low

temperatures, when *spontaneous magnetization* occurs, the magnetization direction defines a preferred direction in space, destroying the rotational invariance. We call this *spontaneous symmetry breaking* and it takes place at the *critical temperature* (for ferromagnets it is the *Curie point*). Since a symmetry is either absent or present, the two phases must be described by different functions of thermodynamic variables, which cannot be continued analytically across the critical point.

Because of the reduction in symmetry, an additional parameter is needed to describe the thermodynamics of the low-temperature phase. This parameter is called the *order parameter*. It is usually an extensive thermodynamic variable. In the case of ferromagnets, the order parameter is the thermal average of the (total) magnetization, $\langle M \rangle$. For the gas-liquid transition, the order parameter is either the volume or the density difference between the two phases. Notice that the density is not an extensive quantity! Notice also that there is no obvious symmetry change in the gas-liquid transition.

The basic idea of phase transitions is that near the critical point, the order parameter is the only relevant thermodynamic quantity.

Some examples of the order parameters and conjugate fields are given in the following table:

Systems	Order Parameter	Conjugate Field
Gas-liquid	$V_G - V_L$	$p - p_c$
Ferromagnets	M	H
Antiferromagnets	$M_{staggered}$	$H_{staggered}$
Superfluids	$\langle \psi \rangle$ (Condensate wave fn.)	Not physical
Superconductors	Δ (Gap parameter)	Not physical

1.5.2 Critical Point

1. *Liquid-gas transitions.* In Figure 1.7(a) a typical phase diagram of a solid-liquid-gas system in the $P-T$ plane at constant V and N is shown. Here we would like to concentrate on the liquid-gas transition. The liquid and the gas phases coexist along a line where the transition between these two phases is first order.

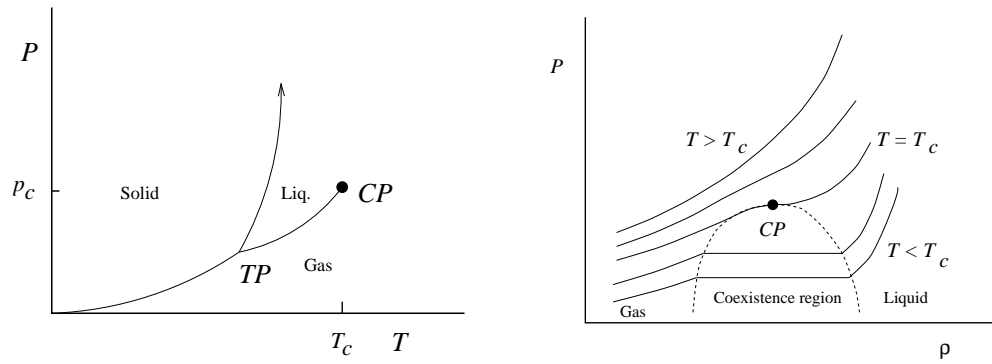


Figure 1.7: Phase diagram of a fluid. CP is the critical point; TP is the triple point.

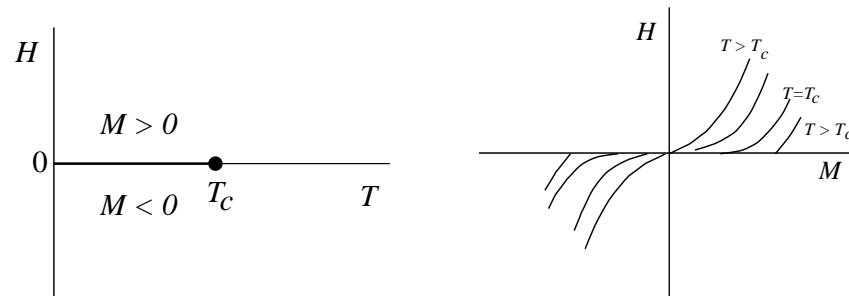


Figure 1.8: Phase diagram of a ferromagnet.

If T is increased, the coexistence line terminates in the *critical point*, where the transition between the two phases is continuous. Beyond the critical point, there is no transition between the two phases, there is no singularity in any physical quantity upon going from one phase to the other. It is also instructive to consider the isotherms in the $P - \rho$ plane at constant T and N , see Fig. 1.7(b). At low temperature, there is a large difference between the gas and liquid densities, ρ_G and ρ_L , but as the critical temperature is approached, this difference tends to zero. The existence of a quantity that is non-zero below the critical temperature and zero above it, is a common feature of critical points in a variety of different physical systems. $\rho_L - \rho_G$ is the *order parameter* for the liquid-gas critical point.

2. *Ferromagnets.* A typical phase diagram of a ferromagnet is shown in Fig. 1.8(a). The order parameter is the magnetization M , i.e., the total magnetic moment. At low temperature, M is ordered either "up" or "down", depending on the external field H . When H changes sign, the system undergoes a first-order phase transition (bold line) in which the magnetization changes its direction discontinuously [Fig. 1.8(b)]. As T is increased, the *critical point* is reached, at which M changes continuously upon variation of H but its derivative with respect to H , i.e., the *susceptibility diverges*. At still higher T , there is no phase transition, the spins are simply disordered, this is the paramagnetic region.

1.5.3 Critical Exponents

In this Section the behaviour of the thermodynamic quantities *near* the critical point is discussed. We suppose that very near the critical point, any thermodynamic quantity can be decomposed into a "regular" part, which remains finite (not necessarily continuous) and a "singular part" that can be divergent or have divergent derivatives. The singular part is assumed to be proportional to some power of $|T - T_C|$ (or $p - p_c$).

Definition of the critical exponents. For clarity, we will define the critical exponents on a ferromagnet. However, their definition will be general and will be valid for arbitrary system that undergoes a continuous phase transition. The most important critical exponents are:

β = *Order parameter exponent.* When $H = 0$, the magnetization M in a ferromagnet is a decreasing function of T and vanishes at T_C (See Fig. 1.9).

For T very close to (but below) T_C , M can be written as

$$M \sim (T_C - T)^\beta. \quad (1.75)$$

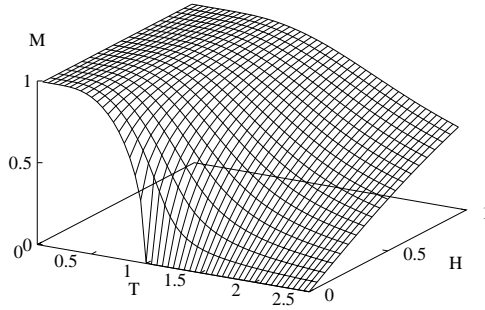


Figure 1.9: Order parameter vs. temperature and field.

β is the *order parameter exponent* which describes the behaviour of M near T_C . Here and later, \sim means "the singular part is proportional to".

$\delta =$ *Exponent of the critical isotherm*. When $T = T_C$, M vanishes for $H = 0$ but increases very rapidly if H increases. For small H , the singular part of M is proportional to:

$$M \sim H^{1/\delta}, \quad (1.76)$$

where $\delta > 1$.

$\gamma =$ *Susceptibility exponent*. As T_C is approached either from above or from below, the susceptibility diverges. The divergence is described with the exponent γ :

$$\chi \sim |T - T_C|^{-\gamma}. \quad (1.77)$$

Notice that the exponent γ is the same for $T > T_C$ and $T < T_C$ whereas the proportionality constants are different.

$\alpha =$ *Specific heat exponent*. The specific heat at constant volume (for ferromagnetic systems one has to take $H = 0$) has a singularity at T_C . This singularity is described by the exponent α :

$$C_V \sim |T - T_C|^{-\alpha}. \quad (1.78)$$

As usually, the exponent α is the same for $T > T_C$ and $T < T_C$ whereas the proportionality constants are different.

$\nu =$ *Correlation length exponent*. As already mentioned, the correlation length ξ is a temperature- dependent quantity. As we shall see later, ξ diverges at the

critical point with the exponent ν :

$$\xi \sim |T - T_C|^{-\nu}. \quad (1.79)$$

$\eta =$ *Correlation function exponent at the critical isotherm*. At T_C , ξ diverges and the correlation function Γ decays as a power law of r ,

$$\Gamma \sim r^{d-2+\eta}, \quad (1.80)$$

where d is the dimensionality of the system.

Scaling. As the name suggests, the scaling has something to do with the change of various quantities under a change of length scale. Important scaling laws concerning the thermodynamic functions can be derived from the simple (but strong) assumption that, near the critical point, the correlation length ξ is the only characteristic length of the system, in terms of which all other lengths must be measured. This is the "scaling hypothesis."

With the aid of the scaling hypothesis we are able to get relations between the critical exponents. The most common scaling relations are:

$$\begin{aligned} \gamma &= \beta(\delta - 1) \\ \gamma &= \nu(2 - \eta) \\ \alpha + 2\beta + \gamma &= 2 \\ \nu d &= 2 - \alpha \end{aligned} \quad (1.81)$$

so that only two of the above exponents are independent. The last four equations are called the *scaling laws*. We shall prove some of the scaling laws later.

Universality. Some quantities depend on the microscopic details of the system. Examples of such quantities are:

- The critical temperature depends on the strength of interaction.
- The proportionality constants (e.g., for the temperature dependence of the magnetization) also depend on the microscopic properties of the system.

On the other hand, the *critical exponents* and the functional form of the equation of state, of the correlation functions, etc. are independent of many details of the system. They depend only on global features, such as:

- The spatial dimensionality,
- symmetry (isotropic, uniaxial, planar,...),

Systems that have the same critical exponents and the same functional form of the equation of state, etc, belong to the same *universality class*. For example,

the Ising model in $d = 2$ forms one universality class, whereas in $d = 3$ it forms another universality class, the Ising models in $d = 2$ and $d = 3$ have different critical exponents because they have different spatial dimensionality. However, on a first glance very different physical systems often belong to the same universality class. Example: binary alloys and some magnetic systems can be described with mathematically similar models and they belong to the same universality class. Roughening of some crystal surfaces at high temperature (but below the melting temperature) and the $d = 2$ Coulomb gas are members of another universality class.